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Novel and Simple Approach to Elimination of
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Photoelectrochemical Systems

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NOVEL AND SIMPLE APPROACH TO ELIMINATION OF DILUTE
TOXIC WASTES BASED ON PHOTOELECTROCHEMICAL SYSTEMS

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of solid and hazardous wastes. These materials, if improperly dealt with, can threaten both public health and the environment. Abandoned waste sites and accidental releases of toxic and hazardous substances to the environment also have important environmental and public health implications. The Hazardous Waste Engineering Research Laboratory assists in providing an authoritative and defensible engineering basis for assessing and solving these problems. Its products support the policies, programs and regulations of the Environmental Protection Agency, the permitting and other responsibilities of State and local governments and the needs of both large and small businesses in handling their wastes responsibly and economically.

This report investigated several basic parameters, important for extending photocatalytic purification of water contaminated with trichloroethylene (TCE), from the laboratory to the field. The adverse effects of low level, long duration ingestion of TCE contaminated water is a problem that is being debated by the technical community.

For further information, please contact the Alternative Technologies Division of the Hazardous Waste Engineering Research Laboratory.

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ABSTRACT

This work investigated several basic parameters, important for extending photocatalytic purification of water contaminated with trichloroethylene (TCE), from the laboratory to the field. Some of these variables strongly influence the decomposition kinetics of the TCE. Parameters investigated were the effect of solution pH, initial TCE concentration, presence of naturally occurring ions, temperature and presence of "color bodies". It was found that the photocatalytic decomposition of aqueous TCE occurs more than twice as fast in the pH range 6.4 to 9 than in the range 3.4 to 5. The rate of TCE decomposition was shown to be strongly dependent on its initial concentration. Photoelectrochemically nonreactive ions such as Ca^{+2} , Mg^{+2} and SO_4^- did not play a measurable role in the reaction. Temperature vs TCE decomposition rate constant data exhibited non-classical dependence by yielding an activation energy of about 2 kcal/mole and a pre-exponential factor of about 1 min^{-1} . The decomposition rate of TCE was not seriously diminished by the presence of 0.059 weight percent of powdered iron oxide color bodies. Additionally, various photocatalyst materials were also tested but titanium dioxide exhibited superior activity in decomposing TCE. In this laboratory study low intensity irradiation having the equivalent intensity of 1/4 to 1/5 Solar at AM1 was employed in order to exemplify the feasibility of large scale water purification utilizing natural solar light.

CONTENTS

	<u>Page</u>
Notice.....	ii
Foreword.....	iii
Abstract.....	iv
Figures.....	vi
Tables.....	vii
1. Introduction.....	1
2. Conclusions.....	3
3. Recommendations.....	4
4. Materials and Method.....	5
5. Experimental Procedures.....	7
6. Results and Discussion.....	11
References.....	21

FIGURES

<u>Number</u>	<u>Page</u>
1. Schematic diagram of the reactor used to demonstrate the photocatalytic decomposition of aqueous TCE.	6
2. Plot of the natural log of fraction of initially 20.8 PPM TCE remaining vs time due to photocatalytic decomposition in the absence of pH buffering (the pH ranged from approximately 3.4 to 5 during a run).	11
3. Plot of the raw chloride ion concentration vs time resulting from the photocatalytic decomposition of 20.8 PPM TCE in pH unbuffered solution.	12
4. Plot of fraction of initially 20.8 PPM TCE remaining vs time resulting from photocatalytic decomposition (pH unbuffered).	12
5. Plot of the natural log of fraction of 20.8 PPM TCE remaining vs time due to photocatalytic decomposition when pH buffered at 6.4 to 9.	13
6. Plot of the raw chloride ion concentration vs time resulting from the photocatalytic decomposition of 20.8 PPM TCE in pH 6.4 to 9 buffered solution.	14
7. Plot of fraction of initially 20.8 PPM TCE remaining vs time resulting from photocatalytic decomposition when pH buffered at 6.4 to 9.	14
8. Plot of fraction TCE remaining vs time for the photocatalytic decomposition of 341 PPM TCE buffered at pH = 9.	16
9. Plot of fraction TCE remaining vs time for the photocatalytic decomposition of 100 PPM TCE buffered at pH = 9.	17

TABLES

<u>Number</u>	<u>Page</u>
1. Chloride calibration data and aliquot analysis for a typical pH unbuffered 20.8 PPM TCE photocatalytic decomposition run.	9
2. Rate constant, k , as a function of pH for the photocatalytic decomposition of initially 20.8 PPM.	15
3. Comparison of TCE concentrations near the end-point of two runs as determined by GC/MS analysis and by an exponentially decaying expression.	15
4. Rate constants for various initial TCE concentrations and the time taken to reduce the initial TCE concentration by an order of magnitude, $t_{1/10}$, employing radiation the equivalent of approximately 1/4 to 1/5 Sun at AM1.	18
5. Tabulation of temperature dependence of the rate constant for the photocatalytic decomposition of 20.8 PPM TCE at 1/4 Sun irradiance.	19

1. INTRODUCTION

IDENTIFICATION OF PROBLEM

Trichloroethylene (TCE) is a ubiquitous soil and ground water contaminant. Its widespread appearance in the United States environment is a result of its popularity as an industrial solvent and casual disposal practices. Once in the soil, its degradation does not occur at an appreciable rate. The action of rain, snow melt and underground waters percolating or passing through the ground gradually cause the dissolution and migration of TCE from the original site of contamination into the general environment. The contaminant plume ends up contributing to ground and surface water contamination far removed from the original dump site.

Trichloroethylene and other halocarbons have been shown to be potentially deleterious to animal health and by extension, human health as a carcinogen and/or mutagen and it is associated with adverse effects on the heart, liver, kidney, immune and nervous system at elevated concentrations [1-13]. The adverse effects of low level, long duration ingestion of TCE contaminated water has most recently and dramatically been litigated [14]. Although the causal relationship between lengthy exposure to extremely small concentrations of TCE and adverse health effects is still being debated by the technical community, clearly it is a problem whose time has come for solution.

PRIOR CLEANUP METHODS

Various methods both chemical and physical in nature have been proposed and tested for the clean-up of volatile organics (VOC's) at disposal sites. The clean-up problem can be divided into two general areas of interest; a) cleansing or removal of soil laden with these organics, and b) cleansing contaminated waters originally derived from these soils. For example, in one method pressurized steam injected beneath the soil was used to volatilize the organic contaminants. The resulting condensate containing the VOC's was further treated with activated charcoal. However, non-optimal adsorption isotherms for the charcoal- aqueous interphase resulted in inefficient transfer of VOC's from the aqueous phase to the charcoal phase. Other methods of extracting the VOC from the soil into an aqueous phase exist but the subsequent problem of their destruction has not yet been surmounted. In a method for removing the aqueous VOC, the contaminated water is vigorously sparged with air. The attempt of the system's highly dispersed aqueous phase to maintain the volatiles equilibrium vapor pressure with the unsaturated air results in efficient transfer of volatiles from the water to the air. Photochemical reaction in the atmosphere supposedly results in the degradation of these volatiles. However, this is tantamount to converting water pollution into an air pollution problem. Clearly, the mitigation of contaminants at the source by the chemical destruction is the best way to guarantee diminution of pollution in the general environment.

PHOTOCATALYTIC CLEANUP METHOD

A new technology, exhibiting dramatic laboratory successes, has been shown to

effect the complete mineralization of aqueous chlorinated hydrocarbons such as trichloroethylene, trichloromethane, carbon tetrachloride, pentachlorophenol and others into carbon dioxide and hydrochloric acid [15 - 18]. In this process solar or artificially UV irradiated semiconductor powders, suspended in the water, photocatalytically oxidize the organic contaminants. Water purification based on this technology has the potential to be uncomplicated and inexpensive. This is because the semiconductor powders only have to be suspended in the water and the suspension provided with sufficient mixing to ensure replenishment of the depleted reactants at the particles' surfaces. Additionally, the powders are inexpensive, recyclable and nontoxic.

The energetic considerations of the process are the following. By absorbing photons having energy equal to or greater than the band gap, the semiconductor creates electron/hole pairs. These carriers can then transfer out of the semiconductor into the surrounding solution to do redox chemistry; alternatively they may recombine, with the photon energy becoming lost to thermalization. In order for chemistry to proceed, the following thermodynamic conditions must be met. (1) The energy levels of the electron acceptor must be below the conduction band edge. (2) The energy levels of the hole acceptor must be above the valence band edge. (3) Redox couples satisfying the above conditions must exist simultaneously. For titanium dioxide (anatase), the valence band edge is at +3.0 V vs NHE [19]. Holes with this energy have oxidation potentials large enough to attack most organic bonds [20]. The electrons are injected at the conduction band edge at -0.3 V vs NHE where dissolved O_2 is first reduced to O_2^- and then undergoes reactions resulting in the production of the powerful oxidizing radical species $HO^\cdot$ and $HOO^\cdot$ [17, 21, 22, 23]. The photoinduced production of the powerful oxidizing holes and $HO^\cdot$ and $HOO^\cdot$ radicals is the reason why titanium dioxide is so effective at photodecomposing such a wide class of organic molecules.

The satisfaction of the above three thermodynamic conditions are necessary but not sufficient to ensure that a given reaction will proceed at an appreciable rate. The oxidation of organic molecules in the presence of O_2 is energetically a "downhill" process and should occur spontaneously. This reaction may not occur if the kinetics are slow. However, in the presence of irradiated, naked titanium dioxide the reactions proceed rapidly.

OBJECTIVES OF THIS STUDY

The experiments in this study were performed with the objective of elucidating the effect of certain basic parameters, on the photocatalytic decomposition of aqueous TCE, expected under field conditions. These variables, temperature, ions derived from dissolved minerals, solution pH, initial TCE concentration and turbidity had not been previously investigated. If these parameters exhibited severe practical restrictions to water purification in the ideal situation existing in this laboratory study, then this would indicate the use of caution in committing future resources to larger scale purification of industrial or municipal water sources by this technology. On the other hand, if this investigation uncovered no serious limitations of the process, with respect to the variables discussed above, then further scaled up studies employing contaminated natural waters or industrial effluents would be appropriate.

2. CONCLUSIONS

EFFECT OF DISSOLVED IONS

There was no measurable effect on the photocatalytic decomposition rate of TCE caused by the presence of Ca^{+2} , Mg^{+2} , and SO_4^{-2} ions in solution having a combined ionic strength of 0.01. The presence of up to about 1.5×10^{-3} M dissolved CO_2 did not appear to impair the decomposition of TCE.

EFFECT OF pH

The photocatalytic decomposition of TCE occurs at twice the rate in the pH range of 6.4 to 9.2 than in the range 3.4 to 5.0.

EFFECT OF TEMPERATURE

The photocatalytic decomposition rate of TCE was not strongly dependent on temperature. For example, increasing the temperature by about 30 °C caused a factor of 1.4 increase in reaction rate. A classical reaction having a 25 kcal/mole activation energy would exhibit approximately a 63 fold increase in reaction rate.

EFFECT OF INITIAL TCE CONCENTRATION

The photocatalytic decomposition rate of aqueous TCE was shown to be strongly dependent on the initial TCE concentration. This means that, although the decomposition rate can be described by an apparent first-order exponentially decaying equation, the reaction is clearly not first-order according to the strictest definition. For example, the values of k for 100 and 20.8 PPM initial TCE concentrations are 0.0169 and 0.0462 min^{-1} , respectively. This means that water contaminated by an initial concentration of 20.8 PPM TCE is purified almost three times as fast as water containing 100 PPM TCE.

NEW MATERIALS AS PHOTOCATALYSTS

The new materials tested for activity in photocatalytically decomposing TCE were Fe_2O_3 , SrTiO_3 , WO_3 , and SrZrO_3 . All of these compounds, except for the latter, have been shown to exhibit photoelectrochemical activity. As photocatalysts for the decomposition of TCE, they were all demonstrated to be less active than TiO_2 by several orders of magnitude.

EFFECT OF 'COLOR BODIES'

By introducing 0.059 wt% of powdered Fe_2O_3 to serve as a potentially interfering 'color body' into the 0.10 wt% TiO_2 slurry, the photocatalytic decomposition rate for TCE was decreased by approximately 32% of the rate for TCE decomposition in the absence of Fe_2O_3 . The decrease in the decomposition rate is attributable to light absorption and scattering by the powdered Fe_2O_3 .

3. RECOMMENDATIONS

The laboratory results discussed above, obtained with TCE spiked deionized water, clearly demonstrate that a potential exists for employing photocatalysis for the removal of TCE from contaminated waters. However, the effects of variable light intensity, reactor design and matrix constituents in naturally occurring waters must be investigated prior to a pilot-scale investigation.

LIGHT INTENSITY DEPENDENCE

The light employed in these experiments had UV intensities approximately one fourth to one fifth of the solar intensity at AM1. It would therefore appear that a photocatalytic purification system could potentially be operated in most parts of the United States. Assuming the absence of diffusion limitation, the TCE decomposition rate should be directly proportional to the light intensity. However, commercial feasibility may strongly depend on exactly how the TCE decomposition rate depends on the UV light intensity. Although this will depend, to a degree, on reactor design the proportionality assumed above should be demonstrated.

REACTOR DESIGN

Diffusion limitation, which occurs when reactants must diffuse through a significant quiescent layer occurring microscopically on the photocatalyst particle or macroscopically within the reactor, must be avoided by the generation of suitable fluid turbulence. The generation of good mixing is energy intensive, however, and will constitute a principal operation expense. Therefore, in order to minimize operating expenses over-mixing in the reactor must be avoided. Rudimentary reactor designs that optimize energy usage for turbulence generation must be investigated.

EFFECT OF MATRIX CONSTITUENTS

An attempt to duplicate some of the water constituents present in naturally occurring water was made in this project. However, it is impossible to duplicate the dissolved minerals, natural organic products resulting from decayed vegetation and other sources, organic and inorganic man-made pollutants, organic and inorganic particulates and other substances which occur in natural waters in the laboratory. Experiments should be performed which ascertain the recyclability of the photocatalyst in various naturally occurring waters. This would be another factor affecting this technology's commercial feasibility. Another concern is the presence of other aqueous organics which could compete with the targeted toxicant for the photogenerated oxidative species that effect decomposition. Therefore, the next logical step is to demonstrate that the photocatalytic decomposition of TCE contained in natural waters occurs at an appreciable rate. This successful demonstration would be a very important advance towards applying this technology to the decomposition of aqueous toxicants that pollute environmental waters.

4. MATERIALS AND METHOD

SEMICONDUCTOR MATERIALS

The photocatalyst, titanium dioxide, employed in this study was obtained from two sources: (1) MCB Manufacturing Chemists, Inc., TX685, lot no. 9M09 and (2) Degussa Corporation, P25 (primary particle average size 0.030 micron diameter with a BET surface area of about 50 m²/g). The reason for switching from the MCB to the Degussa material was because the manufacture of the MCB product had ceased and a reliable reproducible source was desired. The photocatalytic activity of the two materials exhibited no significant difference in activity in decomposing aqueous TCE. In all the experiments performed, the weight of photocatalyst employed was 0.85 g (0.10 weight percent)

The other semiconductor powders investigated for photocatalytic activity in decomposing TCE were strontium titanate, SrTiO₃, (Alfa Products) 99.5% pure with an average particle size of 2 microns; strontium zirconate, SrZrO₃, (Alfa Products) 99% pure; and tungsten trioxide, WO₃. Ferric oxide, Fe₂O₃, was obtained from Atomergic Chemical Corporation 99.999% pure.

PREPARATION OF STOCK SOLUTIONS

Chemicals used for adjusting the solution ionic strength, ionic content, pH adjusting buffers and titers were all reagent grade purity. The concentrations and volumes of solutions added to the reactor were selected to yield a final ionic strength of 0.010. The ionic strength, I , of a fully dissociated electrolyte is given by:

$$I = 1/2 \sum m_i z_i^2 \quad (1)$$

where m is the molality of a given ion and z is the ionic charge. In this work, because of the dilute solutions employed, the molarity M approximates the molality very closely.

The calcium, magnesium and sulfate stock solution was prepared by dissolving 2.83g of Ca(NO₃)₂·4H₂O, 0.790g of MgSO₄ and 2.476g of Na₂SO₄ in 1 L of water in a volumetric flask. Subsequent dilution of 74.5 ml of this stock solution in the 850 ml of reactor water resulted in Ca²⁺, Mg²⁺ and SO₄²⁻ ion concentrations and ionic strength similar to hard-waters found in Boulder, CO. Substituting the diluted concentrations of the ions and their corresponding charges into eq(1) will yield $I = 0.010$.

The 5.00 M sodium nitrate stock solution was prepared by dissolving 42.5g of sodium nitrate in 100 ml of water. A 0.010 M solution was obtained by pipetting 1.70 ml of the stock solution into the reactor and diluting to 850 ml.

The pH buffering (pH = 6.4) stock solution was prepared by dissolving 11.33g of Na₂HPO₄ and 40.26g of KH₂PO₄ in 1 L of water in a volumetric flask.

Dilution of 14.9 ml of this solution in the 850 ml reactor volume yielded a solution ionic strength of 0.010. The pH adjusting (pH = 9.0) buffer stock solution was prepared by dissolving 6.35g of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ in 500 ml of water. This stock solution was diluted 1:10 upon addition to the reactor. In this case the ionic strength of the solution is less than 0.010 because of the incomplete dissociation of the tetraborate salt. This factor should not affect the analysis, because the same borate solution is employed for the calibrating solutions. The kinetics of TCE decomposition should also remain unaffected because ionic strength does not appear to play a significant role over the range used in this and another study [24].

Prior and subsequent to analyzing for solution chloride ions due to TCE decomposition, the electrode was calibrated by immersion in stock hydrochloric acid solutions bracketing the chloride ion concentration expected. These $1.00\text{E}-3$ and $1.00\text{E}-4$ M hydrochloric acid solutions were prepared by diluting 14.00 and 1.40 ml of 0.0714 ± 0.0001 M stock hydrochloric acid solution in 1 L volumetric flasks containing sufficient buffer to make the final ionic strengths equal to 0.011 and 0.010, respectively. The difference in the ionic strength of the two calibration solutions is not considered a problem because this imitates the situation that exists when TCE is decomposed in the presence of the initially 0.010 ionic strength adjuster or pH buffer in the reactor solution.

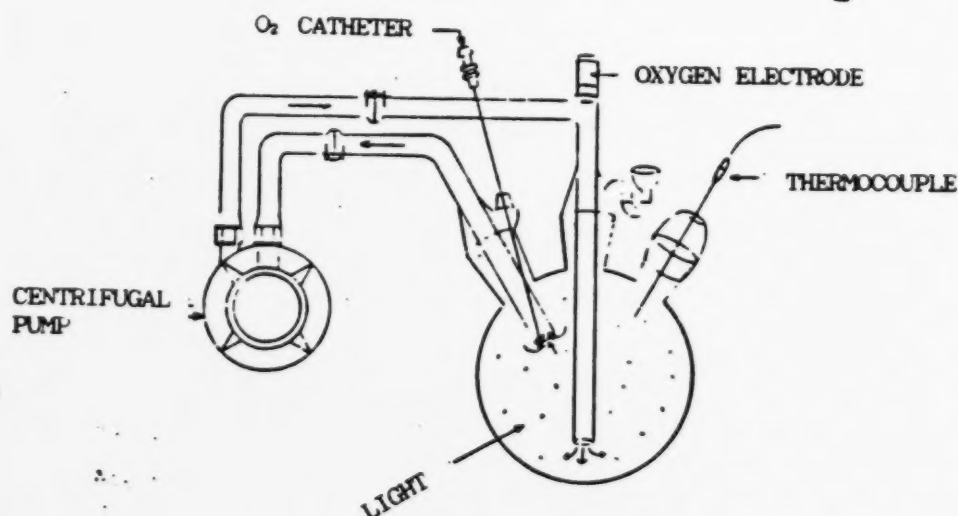


Figure 1. Schematic diagram of the reactor used to demonstrate the photocatalytic decomposition of aqueous TCE.

5. EXPERIMENTAL PROCEDURES

REACTOR

The reactor (Figure 1) employed in these experiments was a 15.2 cm diameter 4.2 cm thick cylinder fitted with three necks on top. Light entered the reactor via a quartz window. Maintenance of powder suspension and mixing were achieved by use of a centrifugal pump. Two of the necks of the reactor served as the inflow and outflow connections to the pump. The third neck was used to add or remove material to the reactor. The total fluid capacity of the system was 850 ml. The irradiated volume was 762 ml, but no correction to the data due to the dark volume was made. Because solution oxygen was consumed during the photocatalytic reaction it had to be supplemented in order for the sustenance of the decomposition reaction. This was achieved by administering high purity oxygen through a fine catheter backed by a micrometer adjusted needle valve. The catheter injected the oxygen directly into the pump inflow line. This resulted in efficient oxygen dissolution assisted by the turbulence within the pump housing. A "T" in the pump outflow line allowed the insertion of the YSI oxygen probe for the continuous monitoring of the slurry oxygen concentration. Maintenance of constant temperature within the reactor was achieved by inserting it in a recirculating water bath also fitted with a quartz window.

LIGHT SOURCE

A 1000 Watt high-pressure Xe lamp outfitted with quartz lenses and a water-IR filter was the light source. Radiation from the lamp passed through a 300 nm cut-off filter. The light intensity impinging on the reactor, in the wavelength interval 300 to 380 nm, was the equivalent of one fourth to one fifth the intensity derived from the sun at Air Mass One (AM1) in this wavelength region. Light having wavelengths only in the 300 to 380 nm interval was employed because wavelengths longer than 380 nm do not produce photocurrents in the 3.3 eV band-gap TiO₂ photocatalyst. By using light with wavelengths no shorter than 300 nm photodechlorination effects are precluded. Additionally, the terrestrial solar spectrum is not significantly intense for wavelengths shorter than 300 nm. The lamp's power supply was held at a 40 A current during all the experiments performed in this study. However, gradual degradation of the bulb resulted in light intensity diminishment as determined by periodic measurement. The data were generally not corrected for this light effect except in the case of the temperature study.

ANALYTICAL METHODS

The photocatalytic decomposition of TCE follows the stoichiometry:



Note, that for 1 mole of decomposed TCE, 3 moles of chloride ion are produced. Because chloride ion is a completed reaction product, following its production yields the true reaction kinetics of TCE decomposition. (In comparison, following TCE decomposition by measuring the disappearance of TCE can lead to certain pitfalls. For example, the disappearance of TCE from solution may result from sparging, owing to its high volatility, rather than its

decomposition.) Obtaining a chloride concentration corresponding to the mass balance of the chlorines present in TCE, unequivocally demonstrates TCE decomposition.

The chloride concentration was followed by periodically removing aliquots for subsequent analysis. Analysis was performed by measuring the potential (Keithley 616 digital electrometer) generated between a HNU chloride specific electrode (No. ISE-30-17-00) vs a double junction calomel reference electrode. This technique for following the oxidation of halogenated hydrocarbons has been widely used in the literature [15, 16, 18]. The procedure is the following: after the reaction is completed, all the aliquots and calibrating solutions are brought to a common temperature by immersion in a water bath. The electrode is calibrated in chloride ion solutions approximately bracketing the background chloride and the expected chloride concentrations resulting from 100% TCE decomposition. This procedure works very well because of the electrode's excellent linearity over several orders of magnitude chloride concentration. For example, in the case of 20.8 PPM TCE, $1.00\text{E-}4$ and $1.00\text{E-}3$ M HCl solutions containing the appropriate concentrations of ionic strength or pH buffer were employed for calibration. A 57 ± 1 mV/decade change in chloride indicates normal electrode response and verification of uncontaminated calibration solutions. The electrode exhibits non-linear response to the log of the chloride ion concentration below about $5\text{E-}5$ M. In cases where the chloride background was below this concentration, it was estimated from carefully determined calibration curves. Extreme care must be taken to avoid contaminating the calibrating solutions or the electrode surfaces with ambient chloride ions. Subsequent to performing chloride analysis on the aliquots, the calibration of the chloride electrode is checked again.

For example, Table 1 below shows the typical data derived from the chloride analysis of a 20.8 PPM TCE run. Complete mineralization of the TCE should yield $4.75\text{E-}4$ M chloride ion concentration. Note that the background chloride concentration at $t=0$, $[\text{Cl}^-]_{\text{back}}$ ($= 4.0\text{E-}5$ M), though small, is not insignificant. It was subtracted from the chloride detected in each of the aliquots, $[\text{Cl}^-]_{\text{meas}}$, to yield the chloride due to TCE decomposition. The molarity of chloride produced from 100% decomposition of a given concentration of TCE in PPM, where 131.4 is the molecular weight of TCE, is:

$$[\text{Cl}^-]_{\text{inf}} \text{ in M} = ([\text{TCE}] \text{ in PPM} \times 3) / (131.4 \times 1000) \quad (3)$$

The fraction of TCE remaining is given by:

$$[\text{TCE}] / [\text{TCE}]_0 = 1 - ([\text{Cl}^-]_{\text{meas}} - [\text{Cl}^-]_{\text{back}}) / [\text{Cl}^-]_{\text{inf}} \quad (4)$$

where $[\text{Cl}^-]_{\text{back}}$ and $[\text{Cl}^-]_{\text{inf}}$ are the background chloride ion concentration and the chloride ion concentration expected due to 100% of the TCE decomposition, respectively. Because a plot of fraction of TCE remaining vs time looks like the exponentially decaying function given by first order kinetics (eq(5)), the data was treated as if first order kinetics obtained. The rate constants, k , obtained in this manner permit ready comparison among many experiments and facilitate their discussion. It is emphasized here, and later on in the discussion, that the TCE decomposition is not first order, but only follows

exponential decay governed by a constant which is a function of the initial TCE concentration.

$$[TCE]/[TCE]_0 = \exp(-k \cdot t) \quad (5)$$

Inspection of eq(5) indicates that a plot of $\ln([TCE]/[TCE]_0)$ vs time should yield a straight line. By performing linear regression on this data, mathematically pinned at $\ln([TCE]/[TCE]_0) = 0$, the constant k was obtained. The data was pinned at $\ln([TCE]/[TCE]_0) = 0$ because it is known that at this point $[TCE]/[TCE]_0$ must be identical to unity (see the first point in Table 1). Mathematical pinning was accomplished by adding an enough 0,0 data points to make the zero intercept insignificant.

TABLE 1. Chloride calibration data and aliquot analysis for a typical pH unbuffered 20.8 PPM TCE photocatalytic decomposition run.

CALIBRATION DATA					
Before Analysis			After Analysis		
[Cl ⁻]		mV	[Cl ⁻]		mV
1.00E-4		203.5	1.00E-4		203.5
1.00E-3		146.5	1.00E-3		146.5

Time (min)	Electrode mV	[Cl ⁻] (M)	[Cl ⁻] _{meas} -[Cl ⁻] _{back} (M)	[TCE]/[TCE] ₀	pH
0	230	4.00E-5	0	1.000	4.92
40	186.5	1.99E-4	1.59E-4	0.666	3.90
100	170.5	3.79E-4	3.39E-4	0.286	3.61
220	163.5	5.03E-4	4.63E-4	0.025	3.41

As stated earlier in this report, the determination of the TCE concentration near the reaction end-point, via chloride analysis alone, is extremely inaccurate because it is based on a calculation involving the subtraction of two large numbers. However, by obtaining the rate constant, k , where the accuracy of the chloride analysis is high and use of eq(5), the TCE concentration near the reaction end-point is predictable. In order to verify the TCE concentration predicted by eq(5), GC/MS analysis employing EPA method 624 was performed for TCE near the end-point of two runs. The analysis was performed by a contract analytical laboratory employing the EPA protocol. This laboratory had participated in several EPA Water Pollution Laboratory Performance Evaluation Studies. In these cases the quality control measures employed were as follows: Samples were placed in specially cleaned VOA bottles obtained from I-Chem Research with special care taken to remove any head space. Samples were submitted with blanks. Samples and blanks were stored refrigerated for no more than a couple of days. The BFB tune, standard, and blank results were within EPA compliance. The surrogate recoveries were also in compliance with EPA requirements for waters analyzed by EPA method 624.

DESCRIPTION OF A TYPICAL RUN

In a typical run, the reactor, pump and connecting tubing were rinsed several times with tap and deionized water. Ionic strength adjuster or pH buffering solution, the photocatalyst and DI water were added to the cell to make the total volume about 850 ml. The contents were brought to constant temperature and air saturation. The mV reading of the oxygen probe corresponding to the oxygen concentration of the air saturated solution was noted. In order to preclude significant TCE sparging during aeration, it was only at this point that TCE was injected into the reactor via a syringe. The violent mixing within the reactor and pump housing effected rapid TCE dissolution. During this time, the Xe lamp was warmed up and allowed to stabilize at maximum power. The lamp shutter was uncovered and the reactor window irradiated. Within a few seconds of irradiation a lowering in the oxygen concentration was evident. Supplemental oxygen had to be added in order to maintain the solution concentration at the equivalent of that due to air saturation. As the reactant (TCE) was consumed, a diminishing rate of supplemental oxygen had to be added. Approximately 12 ml aliquots, for chloride analysis, were removed just prior to irradiation and periodically throughout the run.

6. RESULTS AND DISCUSSION

pH EFFECT ON TCE DECOMPOSITION

pH RANGE 3.4 TO 5

In the following experiments the TCE concentration was 20.8 PPM. A pH adjusting buffer was not used in experiments in which Ca^{+2} , Mg^{+2} , and SO_4^{-2} ions or NaNO_3 was used to adjust the solution ionic strength to 0.010. The time dependence of the pH of the reaction therefore was dictated by the reactants and products arising from the photocatalytic decomposition of the TCE. The data shown in the figures below was obtained from two runs employing the Ca^{+2} , Mg^{+2} , and SO_4^{-2} solution and five runs using the NaNO_3 solution. These experiments have been grouped together because, all other parameters being equal, the pH was the main factor affecting TCE photocatalytic decomposition kinetics. The pH data shown in Table 1 is typical of the decomposition of 20.8 PPM TCE in the absence of pH buffer. The $\ln([\text{TCE}]/[\text{TCE}]_0)$ vs time raw data is shown in Figure 2. Linear regression analysis of the data yielded the best fit straight line having a slope equal to -0.0205 min^{-1} which is $-k$. Figure 3 shows the chloride ion concentration

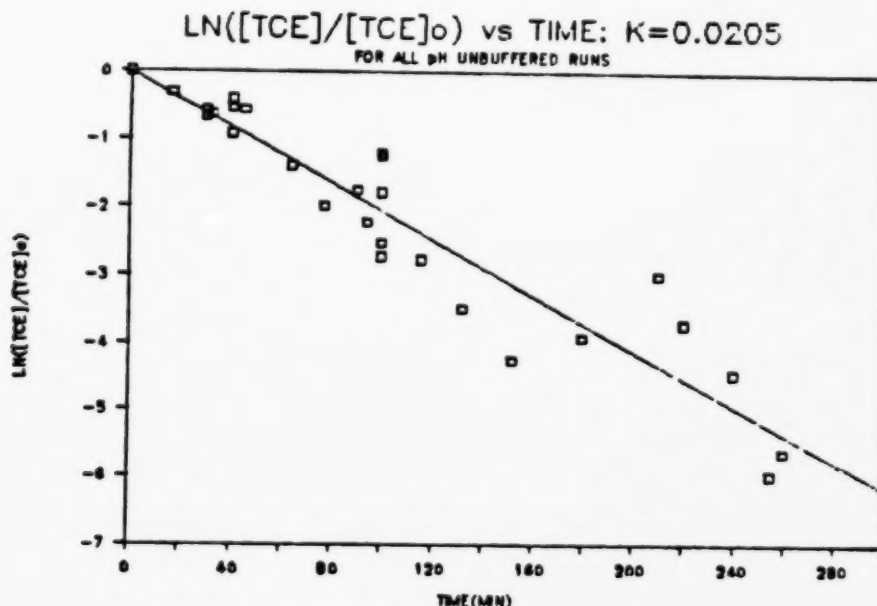


Figure 2. Plot of the natural log of fraction of initially 20.8 PPM TCE remaining vs time due to photocatalytic decomposition in the absence of pH buffering (the pH ranged from approximately 3.4 to 5 during a run).

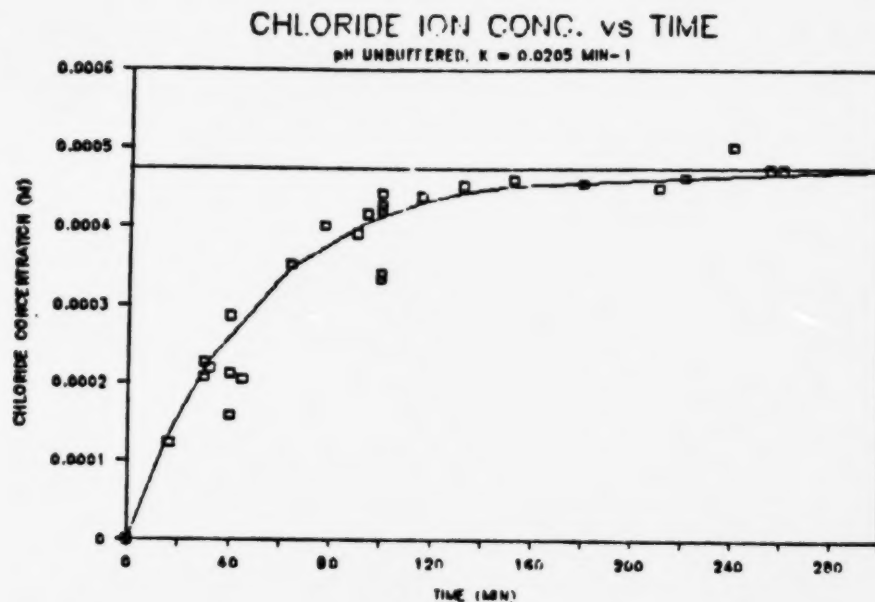


Figure 3. Plot of the raw chloride ion concentration vs time resulting from the photocatalytic decomposition of 20.8 PPM TCE in pH unbuffered solution.

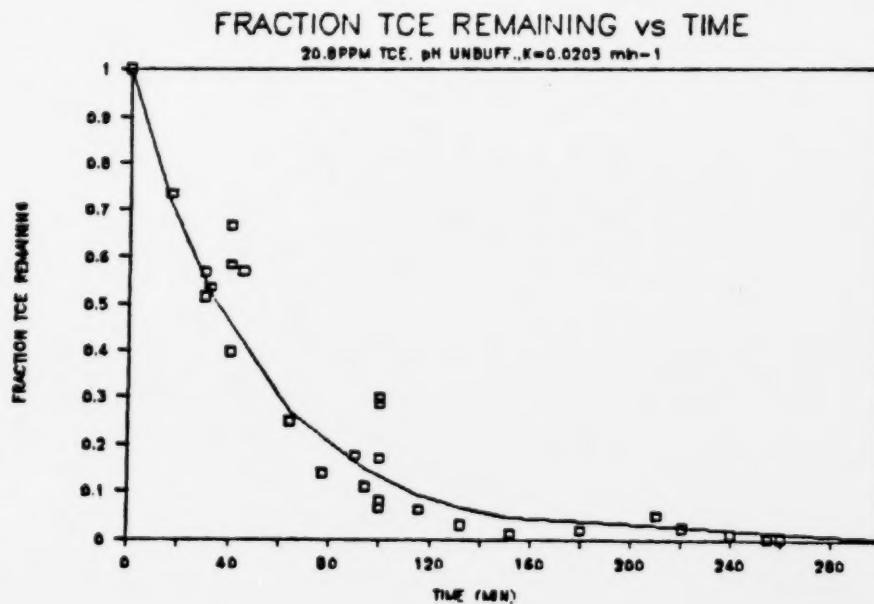


Figure 4. Plot of fraction of initially 20.8 PPM TCE remaining vs time resulting from photocatalytic decomposition (pH unbuffered).

vs time raw data for the photocatalytic decomposition of 20.8 PPM TCE. The smooth curve through the data was calculated using eqs (4) and (5) and the value for $k = 0.0205 \text{ min}^{-1}$. The straight line at the top of the figure represents the chloride concentration due to 100% TCE decomposition. A plot of the data of fraction TCE remaining vs time is shown in Figure 4. The smooth curve was obtained by use of eq(5) and the preceding value for k .

Since no difference in the magnitude of the rate constant could be observed for the reactions run in the presence of Ca^{+2} , Mg^{+2} , and SO_4^{-2} ions and those run with NaNO_3 it is concluded that the nature of the ion is unimportant as long as it does not photoelectrochemically interact with the photocatalyst.

pH RANGE 6.4 TO 9.2

In these experiments phosphate and borate buffers were employed to control the solution pH at about 6.4 and 9.2, respectively. The data exhibited in the figures was derived from three runs made with the 6.4 buffer and two runs with the 9.2 buffer. Within the experimental uncertainties, no difference could be seen between the kinetics of the experiments performed at the two pH ranges. Figure 5 shows the $\ln([\text{TCE}]/[\text{TCE}]_0)$ vs time raw data and the best fit straight line derived from linear regression analysis. A value of $k = 0.0462 \text{ min}^{-1}$ was obtained. Figure 6 shows the raw chloride concentration data and the best fit smooth curve. Figure 7 shows the fraction TCE remaining vs time data and the calculated smooth curve.

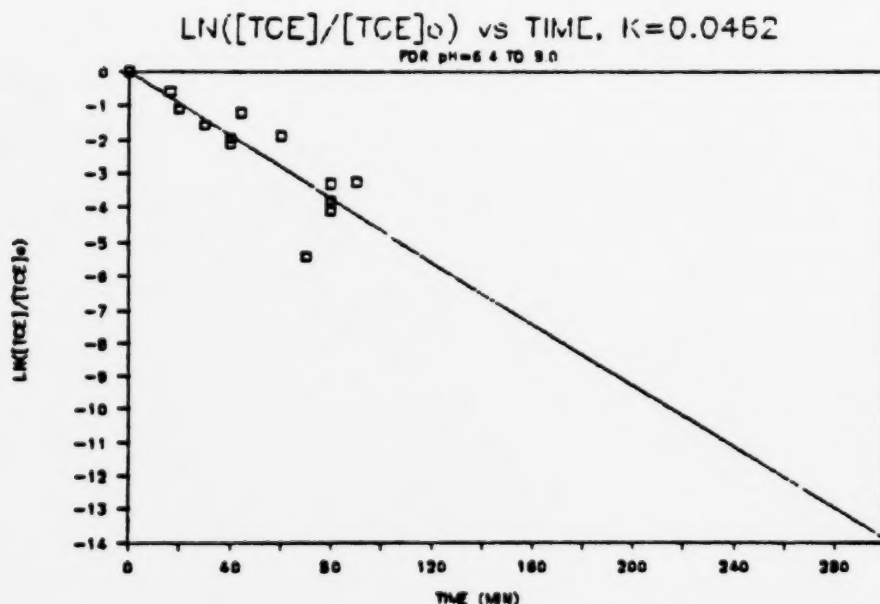


Figure 5. Plot of the natural log of fraction of 20.8 PPM TCE remaining vs time due to photocatalytic decomposition when pH buffered at 6.4 to 9.

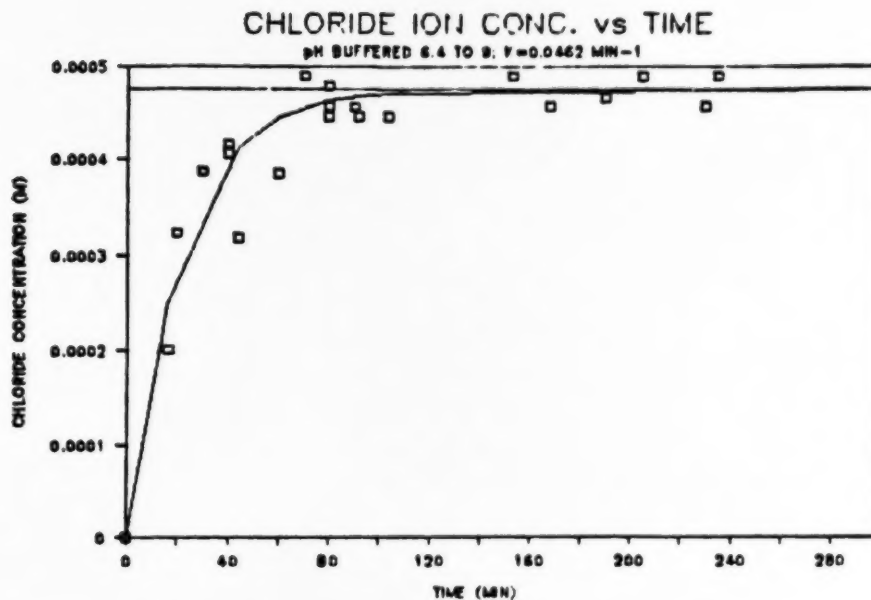


Figure 6. Plot of the raw chloride ion concentration vs time resulting from the photocatalytic decomposition of 20.8 PPM TCE in pH 6.4 to 9 buffered solution.

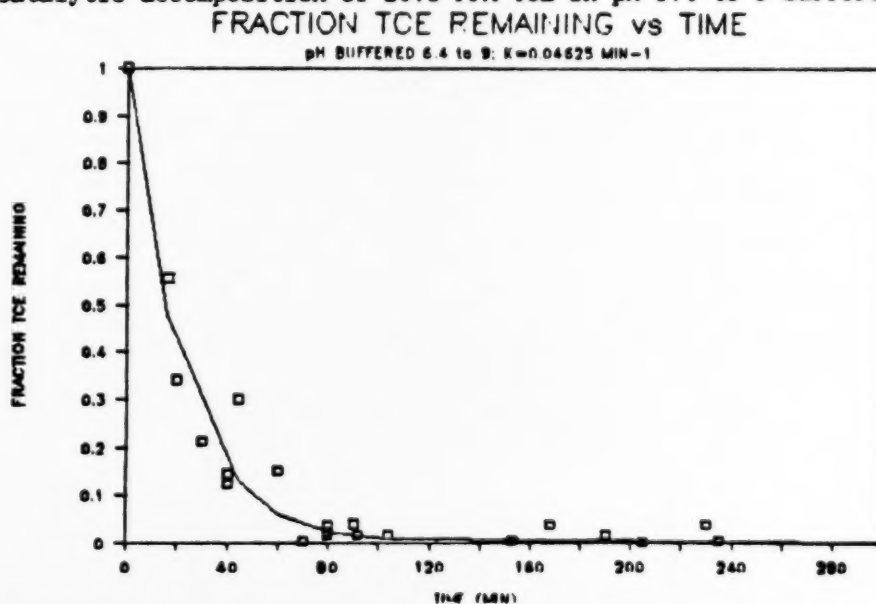


Figure 7. Plot of fraction of initially 20.8 PPM TCE remaining vs time resulting from photocatalytic decomposition when pH buffered at 6.4 to 9.

The results of the experiments investigating the role of pH in the photocatalytic decomposition of TCE are tabulated below. The important result is that the photocatalytic decomposition of TCE occurs over twice as fast in the higher pH than the lower pH range.

TABLE 2. Rate constant, k , as a function of pH for the photocatalytic decomposition of initially 20.8 PPM.

pH range	k (min^{-1})
3.4 to 5	0.0205
6.4 to 9.2	0.0462

RESULTS OF GC/MS ANALYSIS

In order to independently verify that TCE was indeed being photocatalytically decomposed according to the rate expressions discussed above, samples were removed near the end points of runs in the pH range 3.4 to 5 and 6.4 to 9 and subjected to GC/MS analysis via EPA method 624. The results of this analysis and the TCE concentration, predicted by use of eq(5) substituted with the appropriate rate constant values, are exhibited in Table 3. As can be seen, excellent agreement was obtained. Note, that it is undesirable to compare the concentration of TCE remaining derived directly from the chloride ion concentration data. This is because the relative error in the TCE concentration remaining is maximal near the reaction endpoint. This is due to the fact that it is derived from the difference between two large numbers namely, the initial TCE concentration (determined volumetrically) and the chloride ion concentration (determined via the specific ion electrode). The data in Table 2 confirms the accuracy of describing the photocatalytic decomposition of TCE via eq(5) and the rate constant, k .

TABLE 3. Comparison of TCE concentrations near the end-point of two runs as determined by GC/MS analysis and by an exponentially decaying expression.

pH Range	Time (min)	k (min^{-1})	[TCE] by Eq(5) (PPM)	[TCE] by GC/MS (PPM)
3.4 to 5	210	0.0205	0.281	0.360
6.4 to 9	235	0.0462	0.0004	0.001

TCE INITIAL CONCENTRATION EFFECT

Experiments were run employing TCE concentrations of 100 and 341 PPM in order to investigate the effect of initially high TCE concentrations on decomposition kinetics. In the case of these high concentrations there was a large difference between the runs performed in 6.4 and 9.2 pH buffers. This is because the large amounts of HCl produced overcame the buffer capacity of the dilute buffers employed. This moved the kinetics into the slower low pH regime. Only one run using 341 PPM TCE and borate buffer will be reported on.

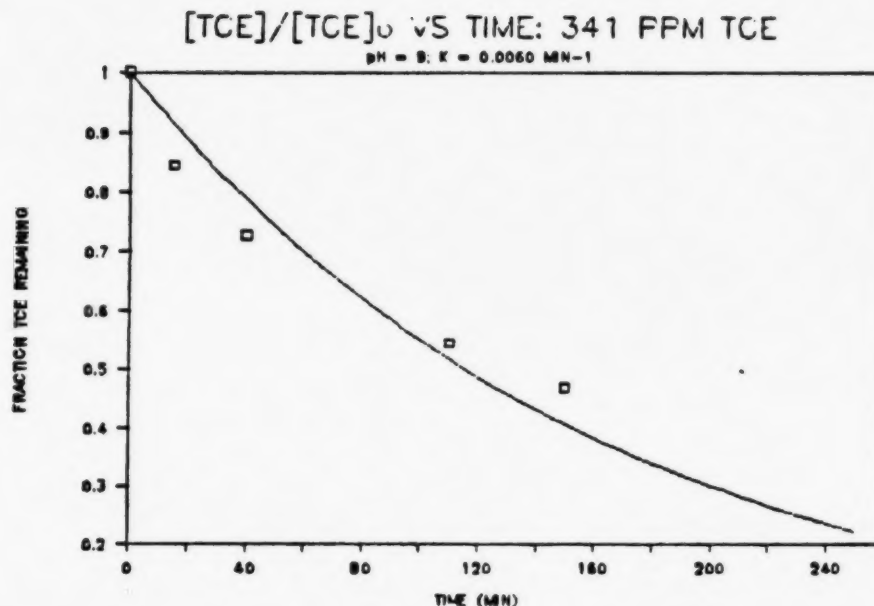


Figure 8. Plot of fraction TCE remaining vs time for the photocatalytic decomposition of 341 PPM TCE buffered at pH = 9.

In this case the initially high pH buffer forestalled a dramatic drop in pH until the reaction was approximately half complete. This initial part of the reaction had a rate constant, $k = 0.006 \text{ min}^{-1}$. Figure 8 shows the fraction of TCE remaining vs time data and the best fit smooth curve calculated by use of eq(5).

Three runs were performed using 100 PPM TCE with the borate buffer. By performing linear regression analysis on the natural log of the fraction TCE remaining data, a rate constant, $k = 0.0169 \text{ min}^{-1}$, was obtained. The fraction of TCE remaining vs time data and the smooth curve calculated by use of eq(5) is shown in Figure 9.

The rate constants for photocatalytic decomposition of TCE at the three initial TCE concentrations discussed above are listed in Table 4 below. These constants apply for reactions run in the high pH regime 6.4 to 9, light intensities approximately one fourth to one fifth the solar intensity at AM1, and in the reactor employed in this study. Also tabulated are the $t_{1/10}$ values which are the time taken for the initial TCE concentration to be reduced by an order of magnitude.

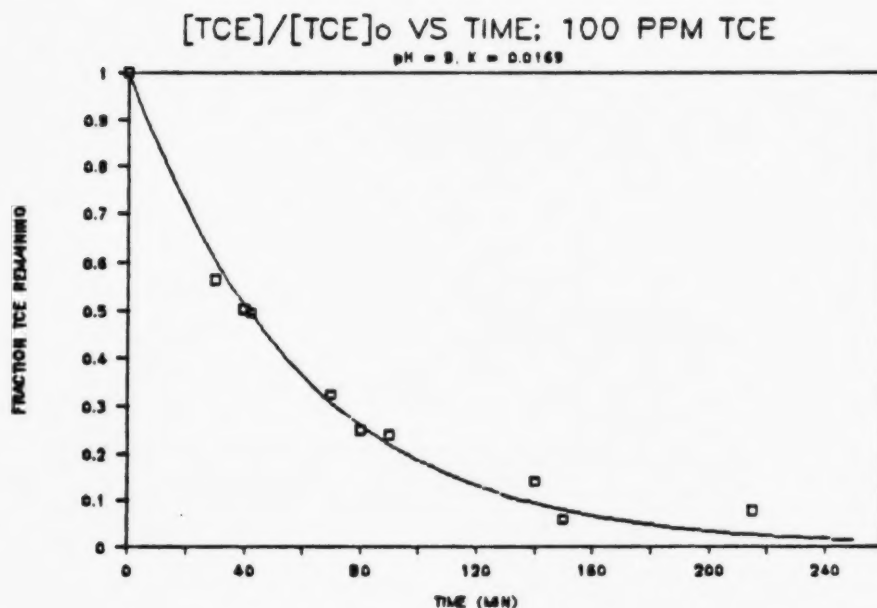


Figure 9. Plot of fraction TCE remaining vs time for the photocatalytic decomposition of 100 PPM TCE buffered at pH = 9.

TABLE 4. Rate constants for various initial TCE concentrations and the time taken to reduce the initial TCE concentration by an order of magnitude, $t_{1/10}$, employing radiation the equivalent of approximately 1/4 to 1/5 Sun at AM1.

[TCE] (PPM)	k (min ⁻¹)	$t_{1/10}$ (min)
341	0.0060	270
100	0.0169	136
20.8	0.0462	50

This result is important because it demonstrates that the rate of photocatalytic decomposition of TCE is strongly dependent on the initial TCE concentration. What it means operationally is the following: if the TCE in an initially 341 PPM solution is photocatalytically decomposed to the point where the TCE has been reduced to 100 PPM, the further decomposition of the TCE will be governed by the rate constant for the 341 PPM solution not the 100 PPM constant. A simple explanation would be that one of the decomposition products, such as chloride ion, is participating in a reaction that competes with other solution species involved in the TCE decomposition reaction. The chloride hypothesis, although not investigated in this work, could be readily tested by decomposing TCE in various concentrations of chloride ions. However, experiments on the photocatalytic decomposition of various organic compounds by one of the authors of this report suggests that this is a general property of the photocatalytic decomposition of all organic molecules [24,25]. Again it must be emphasized, that although the photocatalytic decomposition rate of TCE can be accurately described by a first-order rate expression, the reaction is clearly not first-order because of its dependence on the initial TCE concentration.

TEMPERATURE EFFECT ON TCE DECOMPOSITION

The photocatalytic decomposition of 20.8 PPM TCE was investigated as a function of temperature. The experiments were performed at pH = 9 and a light intensity the equivalent of 1/5 Sun. Three runs were performed at 12°C and two runs at 41.5°C. Linear regression analysis of the fraction TCE remaining data yielded k values of 0.0385 and 0.0532, when corrected to 1/4 Sun, for the two temperatures above, respectively. The correction to 1/4 Sun is necessary in order to allow comparison of the 12°C and 41.5°C experiments, performed at about 1/5 Sun, with the many experiments performed with 20.8 PPM TCE at 26°C at about 1/4 Sun. The variance in intensity is a result of the diminution of the Xe lamp's output as it aged. The normalization of these rate constants was achieved by multiplying them by 5/4. The results, which are tabulated below,

TABLE 5. Tabulation of temperature dependence of the rate constant for the photocatalytic decomposition of 20.8 PPM TCE at 1/4 Sun irradiance.

T (°C)	I (Suns)	k		t _{1/10} (min)
		k (min ⁻¹)	(Normalized to 1/4 Sun) (min ⁻¹)	
12	1/5	0.0308	0.0385	59.9
26	1/4	0.0465	0.0465	46.4
41.5	1/5	0.0426	0.0532	43.3

demonstrate that the reaction is indeed temperature dependent, however this temperature dependence is much less pronounced than would be expected in a classical chemical reaction. Consider the Arrhenius equation, where A is the pre-exponential factor, E_a is the activation energy, R is the gas constant

$$k = A \exp(-E_a/RT), \quad (6)$$

and T is the Kelvin temperature. This equation generally agrees well with the experimental dependence of reaction rate constants on the temperature. Equation 6 implies that a plot of $\ln(k)$ vs $1/T$ should yield a straight line having a slope equal to $-E_a/R$ and a zero-intercept equal to A. Treating the data in Table 5 in this manner yielded a value of $E_a = 2.0$ kcal/mole and $A = 1.3 \text{ min}^{-1}$. Classical chemical reactions usually exhibit values for E_a about one order of magnitude larger than 2 kcal/mole and values for A are of the order 10^{15} min^{-1} and greater. A classical reaction performed at 41.5°C and having a nominal 25 kcal/mole activation barrier, could be expected to run about 63 times faster than when run at 12°C. For the photocatalytic decomposition of TCE only a 1.38 increase in rate is observed. These values, considered anomalous classically, simply reflect the probability that, because this is a photocatalytic reaction, the activation energy for the rate determining step is not provided by thermal processes.

NEW MATERIALS AS PHOTOCATALYSTS

The photocatalytic decomposition of TCE employing photocatalyst powders other than TiO₂ was attempted. The photocatalyst tried were Fe₂O₃, SrTiO₃, SrZrO₃, and WO₃. Of these materials, only WO₃ exhibited measurable activity by decomposing 0.45% of an initially 20.8 PPM TCE solution in 45 minutes. In comparison, TiO₂ decomposed 89% of the TCE. The other materials, except for the SrZrO₃, have exhibited photocurrents in literature studies, however. There are several possible explanations for the lack of measurable activity of these compounds, some of which are as follows: high recombination rates due to the existence of high concentrations of trapping sites resulting from insufficient material purity; mismatch between the semiconductor band energies and the redox potential of a critical intermediate in the TCE decomposition; excluded

from participating in necessary surface catalytic effects that facilitate TCE decomposition due to the nature of their different chemical composition. Clearly, TiO_2 is the best photocatalyst investigated to date for effecting the decomposition of aqueous TCE.

EFFECT OF 'COLOR BODIES'

The introduction of 0.059 wt% of powdered Fe_2O_3 , to serve as a potentially interfering "color body" into the 0.10 wt% TiO_2 slurry, caused approximately a 32% decrease in the TCE decomposition rate. Because such highly light absorbing particulates can be readily removed by conventional filtration techniques, 'color bodies' of this type are not considered a severe limitation towards operating a photocatalytic purification system. However, if logistics preclude their removal prior to purification, this demonstration shows that they will not drastically reduce system efficiency.

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